WSC – CAM – III B

Quality Assurance and Quality Control Requirements for ***SW-846 Methods 7470A and 7471A, Mercury in Liquid Waste and Mercury in Solid or Semi-Solid Waste (Manual Cold-Vapor Technique)*** for the Massachusetts Contingency Plan (MCP**)**

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III. Metal Analysis

B. Quality Assurance and Quality Control Requirements and Performance Standards for SW-846 Methods 7470A and 7471A, Mercury in Liquid Waste and Mercury in Solid or Semi-Solid Waste (Manual Cold-Vapor Technique)

B.1 TABLE OF CONTENTS

Section	Title	Page
1.0	QA/QC Requirements for SW-846 Methods 7470A and 7471A	3
	1.1 Overview of Methods	3
	1.2 General QA/QC Requirements for SW-846 Methods 7470A and 7471A	5
	1.3 Specific QA/QC Requirements and Performance Standards for SW-846 Methods 7470A and 7471A	6
2.0	Data Usability Assessment for SW-846 Methods 7470A and 7471A	12
3.0	Reporting Requirements for SW-846 Methods 7470A and 7471A	12
	3.1 General Reporting Requirements for SW-846 Methods 7470A and 7471A	12
	3.2 Specific Reporting Requirements for SW-846 Methods 7470A and 7471A	12
4.0	Regulatory Limits for Mercury under 310 CMR 40.000	13

List of Tables, and Appendices

Number	Title	Page
Table III B-1	Performance Requirements for SW-846 Methods 7470A and 7471A	8-11
Table III B-2	Routine Analytical Reporting Requirements for SW-846 Methods 7470A and 7471A	13
Appendix III B-1	Sample Collection, Preservation and Handling Procedures for Mercury in Liquid Waste and Mercury in Solid or Semi-Solid Waste (Manual Cold-Vapor Technique)	14

1.0 QA/QC Requirements for SW-846 Methods 7470A and 7471

1.1 Overview of Methods

1.1.1 SW-846 Method 7470A Mercury in Liquid Waste

SW-846 Method 7470A is a cold-vapor atomic absorption (CVAA) procedure for determining the concentration of mercury in mobility-procedure extracts, aqueous wastes, surface and ground waters. Prior to analysis, the liquid samples must be pretreated according to the procedure described in Section 7.0 of this method.

Quantitation is based on the absorption of radiation at 253.7-nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration. The typical aqueous detection limit for this method is 0.0002 mg/L (0.2 µg/L).

Sample preservation, container and analytical holding time specifications for surface water, groundwater, soil, and sediment matrices for metals analyzed in support of MCP decision-making are presented in Appendix III B–1 of this document and Appendix VII-A, WSC-CAM–VII A, "Quality Assurance and Quality Control Guidelines for the Acquisition and Reporting of Analytical Data in Support of Response Actions Conducted Under the Massachusetts Contingency Plan (MCP)".

1.1.2 SW-846 Method 7471A MERCURY IN SOLID OR SEMISOLID WASTE

SW-846 Method 7471A is also a CVAA procedure based on the absorption of radiation at 253.7-nm wavelength by mercury vapor, approved for determining total mercury (organic and inorganic) in soils, sediments, bottom deposits, and sludge-type materials. For routine MCP mercury analyses in solid or semisolid waste, a 0.2-gram sample (dry-weight basis) is subjected to an appropriate dissolution step, as described in Section 7.0 of the Method, prior to analysis. It should be noted, that if the selected dissolution procedure is not sufficient to dissolve a specific matrix type or sample, then this method is not applicable for that matrix.

Because of this small sample (0.2-grams, as recommended in Section 7.1, of the Procedure), "as-received" field samples of solid or semisolid materials must be thoroughly homogenized in the laboratory prior to mercury analysis to obtain a representative aliquot for analysis. If mercury is a contaminant of concern (COC) at an MCP site or if poor precision and/or accuracy (that would adversely effect MCP decision making) associated with sample matrix heterogeneity is anticipated, then the following preemptive or corrective measures should be considered by the LSP:

- Direct the laboratory to use a larger sample aliquot (up to 10 grams) to enhance sensitivity and/or precision. The laboratory must adjust the concentration/volume of all reagents to accommodate the analytical requirements of the larger sample aliquot and re-demonstrate applicable laboratory-specific QC control limits and performance criteria;
- Direct the laboratory to prepare and analyze replicate 0.2-gram aliquots (two or more) for each field sample to better assess variability, associated with sample matrix heterogeneity;
- Utilize more effective field sample homogenization procedures (prior to submitting sample to laboratory for mercury analysis); and/or
- Increase frequency of field duplicates.

If overall site heterogeneity for mercury is a specific concern (i.e. distribution of mercury contamination is inconsistent with the conceptual site model), it is recommended that the number of field samples be increased to improve the representativeness of mercury results for site assessment and characterization.

SW-846 Method 7471A Mercury In Solid Or Semisolid Waste Analytical Notes:

For routine MCP Mercury analysis of solid or semisolid samples, the Department does not require the analysis of triplicate sample aliquots for each determination as described in SW-846 Method 7471A, Section 7.1, Sample Preparation. Consistent with the requirements of 310 CMR 40.0017(1), mercury analysis must be scientifically valid and defensible, and of a level of precision and accuracy commensurate with its stated or intended use. The requirement for triplicate analysis for every determination is overly burdensome for most MCP applications. However, replicate analyses may be warranted in some cases to evaluate sample matrix heterogeneity, at the discretion of the LSP.

1.1.3 SW-846 Methods 7470A and 7471A Interferences

Samples submitted to a laboratory for trace metal analysis may become contaminated by numerous routes during both sampling and analysis. Potential sources of contamination may include:

- Metallic or metal-containing containers and sampling equipment,
- Laboratory acids or reagents,
- Improperly cleaned or stored equipment , and
- Atmospheric inputs such as dirt and dust

Other potential contaminants and their recommended corrective measures, as appropriate, are listed below:

- Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/Kg of sulfide, as sodium sulfide do not interfere with the recovery of inorganic mercury added to reagent water.
- Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253.7 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL).
- Certain volatile organic materials that absorb at the optimum analytical wavelength (253.7 nm) may also cause interference at elevated concentrations. A preliminary run without reagents should determine if this type of interference is present.
- Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/Kg have been shown to have no effect on recovery of mercury from spiked samples.

1.2 General QA/QC Requirements for SW-846 Methods 7470A and 7471A

Each laboratory that uses SW-846 Methods 7470A and 7471A is required to operate a formal quality assurance program to demonstrate the precision and bias of the method as performed by the laboratory and procedures for determining the method reporting limit (RL). The minimum requirements of this program consist of an initial demonstration of laboratory proficiency, ongoing analysis of standards and blanks as a test of continued performance, and the analysis of laboratory control spikes (LCSs) and matrix spikes (MS), to assess accuracy and/or precision. Matrix duplicates or matrix spike duplicates (MSD) may also be used to evaluate precision when such samples are analyzed either at discretion of laboratory or at request of data-user.

The minimum requirements of this program consist of an initial demonstration of laboratory proficiency, ongoing analysis of standards and blanks as a test of continued performance, and the analysis of laboratory control samples (LCSs), and LCS duplicates to assess accuracy and/or precision. Project-specific matrix duplicates or matrix spike duplicates (MSDs) may be used in lieu of LCS duplicates to evaluate precision when such samples are analyzed either at discretion of laboratory or at request of data-user.

Laboratories must document and have on file an Initial Demonstration of Proficiency for each combination of sample preparation and determinative method being used. These data must meet or exceed the performance standards as presented in Section 1.4 and Table III A-1 of this method. Procedural requirements for performing the Initial Demonstration of Proficiency can be found in SW-846 Chapter One, Section 4.4.1 and SW-846 Methods 7470A and 7471A, Section 8.0. The data associated with the Initial Demonstration of Proficiency must be kept on file at the laboratory and made available to potential data-users on request. The data

associated with the Initial Demonstration of Proficiency for SW-846 Methods 7470A and 7471A must include the following:

QC Element	Performance Criteria
Initial Calibration	WSC-CAM-III B, Table III B-1
Continuing Calibration	WSC-CAM-III B, Table III B-1
Method Blanks	WSC-CAM-III B, Table III B-1
% Percent Recovery for MS/LCS	WSC-CAM-III B, Table III B-1
Relative Percent Difference (RPD) for MSD/LCS Duplicate	WSC-CAM-III B, Table III B-1
Other Instrument QC Samples	WSC-CAM-III B, Table III B-1

It is essential that laboratory-specific performance criteria for LCS, LCS duplicates (or project-specific matrix duplicates or matrix spike duplicates, see Table III B-1) and the other data quality indicators, listed in Table III B-1, also be calculated and documented. When experience indicates that the criteria recommended in specific methods are frequently not met for some analytes and/or matrices, the in-house performance criteria will be a means of documenting these repeated exceedances. Laboratories are encouraged to actively monitor pertinent quality control performance standards described in Table III B-1 to assess analytical trends (i.e., systematic bias, etc) and to improve overall method performance.

For SW-846 Methods 7470A and 7471A, laboratory-specific control limits must meet or exceed (demonstrate less variability than) the performance standards for each QC element listed on Table III B-1. It should be noted that the performance standards listed in Table III B-1 are based on multiple-laboratory data, which are in most cases expected to demonstrate more variability than performance standards developed by a single laboratory. Laboratories are encouraged to continually strive to minimize variability and improve the accuracy and precision of their analytical results. The LSP will utilize this analytical performance data to verify that the results reported by the laboratory are consistent with the pre-established data quality objectives for the disposal site.

Use of this method is restricted to use by, or under the supervision of, analysts who are knowledgeable of cold-vapor atomic absorption spectrophotometry as a quantitative tool and the correction of spectral, chemical, and physical interferences described in this method.

1.3 Specific QA/QC Requirements and Performance Standards for SW-846 Methods 7470A and 7471A

Specific QA/QC requirements and performance standards for SW-846 Methods 7470A and 7471A are presented in Table III B-1. Strict compliance with the QA/QC requirements and performance standards for this method, as well as satisfying other analytical and reporting requirements will provide a data user with “Presumptive Certainty” regarding the usability of

analytical data to support MCP decisions. The concept of "Presumptive Certainty" is explained in detail in Section 2.0 of WSC-CAM-VII A.

While optional, parties electing to utilize these protocols will be assured of "Presumptive Certainty" of data acceptance by agency reviewers. In order to achieve "Presumptive Certainty", parties must:

(a) Comply with the procedures described and referenced in WSC-CAM–III B;

(b) Comply with the applicable QC analytical requirements prescribed in Table III B-1 for this test procedure;

(c) Evaluate, and narrate, as necessary, compliance with performance standards prescribed in Table III A-1 for this test method; and

(d) Adopt the reporting formats and elements specified in the CAM

In achieving the status of "Presumptive Certainty", parties will be assured that analytical data sets:

- ✓ Will satisfy the broad QA/QC requirements of 310 CMR 40.0017 and 40.0191 regarding the scientific defensibility, precision and accuracy, and reporting of analytical data;
- ✓ May be used in a data usability assessment, and if in compliance with all MCP Analytical Method standards, laboratory QC requirements, and field QC recommended limits and action levels, the data set will be considered useable data to support site characterization decisions made pursuant to the MCP; and
- ✓ May be used to help support a data representativeness assessment.

Widespread adherence to the "Presumptive Certainty" approach will promote inter-laboratory consistency and provide the regulated community with a greater degree of certainty regarding the quality of data used for MCP decision-making. The issuance of these requirements and standards is in no way intended to preempt the exercise of professional judgement by the LSP in the selection of alternative analytical methods. However, parties who elect not to utilize the "Presumptive Certainty" option have an obligation, pursuant to 310 CMR 40.0017 and 40.0191(2)(c), to demonstrate and document an overall level of (laboratory and field) QA/QC, data usability, and data representativeness that is adequate for and consistent with the intended use of the data.

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Required QA/QC	Data Quality Objective	Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Preparation of Samples	Accuracy and Representativeness	All aqueous and solid samples must be prepared (digested) prior to analysis. See Methods 7470 and 7471 for details. Note: MADEP requires only 1 preparation for each field sample to generate a reportable result.	No	See section 2.1.2 in this guidance for further details on obtaining representative soil results.	
Initial Calibration	Laboratory Analytical Accuracy	(1) Frequency - Daily prior to sample analysis (2) Minimum of a calibration blank plus five calibration standards (3) Linear curve fit with correlation coefficient $r \geq 0.995$. Second order curve fit may be used if $r \geq 0.995$.	No	Re-calibrate as required by method.	
Initial Calibration Verification (ICV)	Laboratory Analytical Accuracy	(1) Frequency - Daily immediately after initial calibration (2) Separate-source from calibration standards (3) ICV % recovery must be 90-110%;	No	Re-calibrate/Re-analyze ICV as required by method	Suspend all analyses until Initial Calibration non-conformance is rectified.
Initial Calibration Blank (ICB)	Laboratory Analytical Sensitivity (instrument drift and contamination evaluation)	(1) Frequency - Daily immediately after ICV (2) Must be matrix-matched (the same concentration of acids as standards and samples) (3) ICB must be < RL	No	Re-calibrate/Re-analyze ICB as required by method	

Required QA/QC	Data Quality Objective	Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Low Level Calibration Check Standard	Laboratory Analytical Sensitivity (to support the RL)	Only required if NOT including the RL as the low-level standard in the calibration curve. (1) Frequency - Daily prior to field sample analysis (2) Check Standard at the level of the RL for mercury (3) % recovery recommended 70-130%	No	Re-calibrate / narrate	Narrate non-compliance.
Continuing Calibration Verification (CCV)	Laboratory Analytical Accuracy	(1) Frequency - Every 10 samples and at end of run (2) Same-source as calibration standards; near mid-point of linear range (3) CCV % recovery must be 80-120%	No	Re-calibrate/Re-analyze all samples since last compliant CCV.	Narrate non-compliance.
Continuing Calibration Blank (CCB)	Laboratory Analytical Sensitivity (instrument drift and contamination evaluation)	(1) Frequency - Every 10 samples and at end of run immediately after CCV (2) Must be matrix-matched (the same concentration of acids as standards and samples) (3) CCB must be < RL	No	Re-calibrate/Re-analyze all samples since last compliant CCB.	Narrate non-compliance.
Method (Preparation) Blank	Laboratory Method Sensitivity (contamination evaluation)	(1) Frequency - One per digestion batch of < 20 field samples. (2) Must be matrix-matched (the same concentration of acids as calibration and QC standards) and digested with the samples (3) Method Blank must be < RL	Yes	Re-digest/Re-analyze all associated samples unless all detected results are > 10x method blank level.	Narrate non-compliance.

Required QA/QC	Data Quality Objective	Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Laboratory Control Sample (LCS)	Laboratory Method Accuracy	(1) Frequency - One per digestion batch of < 20 field samples. (2) LCS must be matrix-matched (aqueous or solid) to field samples, and digested with the samples. (3) LCS % recovery for mercury must be 80-120% for aqueous media and vendor control limits (95% confidence limits) for solids.	Yes	Re-digest/Re-analyze all associated samples.	Narrate non-compliance. Note: MADEP modification to frequency of LCS for consistency with other methods.
LCS Duplicate	Laboratory Method Precision	(1) Frequency - One per digestion batch of ≤ 20 field samples. If samples are undigested (dissolved metals) an ICV duplicate may be substituted for an LCS duplicate. (2) Prepared using same standard source and concentration as LCS. (3) Recommended to be run immediately after LCS in analytical sequence. (4) LCS duplicate must be matrix-matched to samples (aqueous/solid) and digested with the samples (5) Laboratory–determined Relative Percent Difference (RPD) must be ≤ 20 (aqueous) and ≤ 30 (solids), and (6) A project-specific MD or MSD may be substituted to evaluate precision in lieu of an LCS duplicate.	Yes	Recalculate RPD; Locate source of problem; Narrate non-conformances	(1) Locate and rectify source of non-conformance before proceeding with the analyses of subsequent sample batches. (2) Narrate non-conformances

Required QA/QC	Data Quality Objective	Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Project Specific Matrix Spike Sample (MS)	Method Accuracy in Sample Matrix	(1) Frequency - One per digestion batch of < 20 field samples. (2) MS % recoveries must be between 75 – 125 for all matracies (3) Laboratories are expected to develop their own in-house control limits for each media, which should fall within the limits listed above.	Yes Only when requested by the data-user	No corrective action required.	Narrate non-compliance
Project-specific Matrix Duplicate Sample (MD) or Matrix Spike Duplicate (MSD)	Method Precision in Sample Matrix	(1) Frequency - One per digestion batch of < 20 field samples. (2) MSD relative percent difference (RPD) criteria: aqueous results: $\pm$ 20%; soil and sediment results: $\pm$ 35%.	Yes Only when requested by the data-user	No corrective action required.	Narrate non-compliance
General Reporting	NA	(1) Non-detected values must be reported with the sample-specific reporting limit for each ICP analyte. (2) The RL must be $\leq$ the applicable regulatory compliance standard for each metal reported (3) The RL must be verified at least daily with a low-level calibration check standard following the calibration curve or supported by the low-level standard in the calibration curve. (4) Results for soils/sediments must be reported on a dry weight basis for comparison to MCP regulatory standards (5) Sample concentrations that exceed the highest calibration standard must be diluted (in the same acid matrix) to fall within the calibration range when re-analyzed	Yes	Not applicable.	

2.0 Data Usability Assessment for SW-846 Methods 7470A/7471A

Overall data usability is influenced by uncertainties associated with both sampling and analytical activities. This document provides detailed quality control requirements and performance standards for SW-846 Methods 7470A/7471A which may be used to assess the analytical component of data usability. The sampling component of data usability, an independent assessment of the effectiveness of sampling activities to meet data quality objectives, is not substantively addressed in this document.

Note to data users: Consistent with USEPA Region I data validation guidance, the Department requires rejection of non-detected metals results with <30% MS recovery. If Mercury MS % recovery is < 30%, and non-detected results were found, the LSP should consider the use of one or more of the following actions to assess and /or overcome the sample matrix effect encountered:

1) Re-homogenize sample. Prepare and analyze a new sample/MS pair;
2) Perform method of standard additions for quantitation;
3) Perform serial dilution; and/or
4) Perform post-digestion spike.

3.0 Reporting Requirements for SW-846 Methods 7470A and 7471A

3.1 General Reporting Requirements for SW-846 Methods 7470A and 7471A

General reporting requirements for analytical data used in support of assessment and evaluation decisions at MCP disposal sites are presented in WSC-CAM-VIIA. This guidance document provides recommendations for field QC, as well as the required content of the Environmental Laboratory Report, including

- Laboratory identification information presented in CAM-VII A, Section 2.4.1,
- Analytical results and supporting information in CAM-VII A, Section 2.4.2,
- Sample- and batch-specific QC information in CAM-VII A, Section 2.4.3,
- Laboratory Report Certification Statement in CAM-VII A, Section 2.4.4,
- Copy of the Analytical Report Certification Form in CAM-VII A, Exhibit VII A-1,
- Environmental Laboratory Case Narrative contents in CAM-VII A, Section 2.4.5,
- Chain of Custody Form requirements in CAM-VII A, Section 2.4.6

3.2 Specific Reporting Requirements for SW-846 Methods 7470A and 7471A

Specific analytical reporting requirements for SW-846 Methods 7470A/7471A are presented in Table III B-1, Specific QA/QC Requirements and Performance Standards for SW-846 Method 7470A and 7471A and are summarized below in Table III B-2 as "Required Analytical Deliverables (**YES**)". These routine reporting requirements should always be included as part of the laboratory deliverable for this method. It should be noted that although certain items are not specified as "Required Analytical Deliverables (**NO**)", these data are to be available for review during an audit and may also be requested on a client-specific basis.

Table III B-2 Routine Analytical Reporting Requirements for SW-846 Methods 7470A/7471A

Parameter	Required Analytical Deliverable
Initial Calibration	***NO***
Initial Calibration Verification (ICV)	***NO***
Initial Calibration Blank (ICB)	***NO***
Low Level Calibration Check standard	***NO***
Continuing Calibration Verification (CCV)	***NO***
Continuing Calibration Blank (CCB)	***NO***
Method (Preparation) Blank	***YES***
Laboratory Control Standard (LCS)	***YES***
LCS Duplicate (or project-specific MD or MSD)	***YES***
Field Matrix Spike Sample (MS)	***YES, only if requested by the LSP***
Field Matrix Duplicate (MD)	***YES, only if requested by the LSP***
Field Matrix Spike Duplicate (MSD)	***YES, only if requested by the LSP***
General Reporting	***YES*** [1]

1. Non-detected values must be reported with the sample-specific reporting limit.

4.0 Regulatory Limits for Mercury under 310 CMR 40.000

The most stringent (lowest) MCP Reportable Concentrations (RCs) and Method 1 Standards for mercury are as follows:

MCP Regulatory Criteria	Concentration
RC GW-1	0.001 mg/L (ppm)
RC S-1	20 mg/kg (ppm)
Groundwater Method 1 GW-3 Standard	1 µg/L (ppb)
Method 1 Soil Category S-1 & GW-1 Standard	20 µg/g (ppm)

Sample preservation, container and analytical holding time specifications for surface water, groundwater, soil, and sediment matrices for mercury analyses conducted in support of MCP decision-making are summarized below and presented in Appendix VII-A of CAM-VII A, Quality Assurance and Quality Control Guidelines for Sampling, Data Evaluation, and Reporting Activities for the Massachusetts Contingency Plan (MCP). Additional guidance may be found in SW-846, Chapter Three. Containers used for the collection of samples for the determination of Mercury should be pre-washed with detergent, acid washed and final rinsed with reagent grade water.

Sample Matrix	Container [1]	Preservation	Holding Time [2]
Aqueous Total Mercury	500 mL glass or Polyethylene Bottle	HNO_3 to pH < 2,	28 days
Aqueous Dissolved Mercury	500 mL glass or Polyethylene Bottle	Filter (0.45 µm) on site; or at the laboratory ***(prior to acid preservation)*** within 24 hours of collection HNO_3 to pH <2,	28 days
Soil and Sediments	(1) 4-ounce glass jar with teflon-lined cap	Cool, 4°C	28 days
Concentrated Waste Samples	125 mL wide mouth glass or plastic	Cool to 4°C	28 days

1 The number of sampling containers specified is not a requirement. For specific analyses, the collection of multiple sample containers is encouraged to avoid resampling if sample is consumed or compromised.
2 From date of sample collection.